

Metal–silicate partitioning and the incompatibility of S and Si during core formation

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Abstract

We have determined the partitioning of a number of siderophile and lithophile elements between liquid metal and liquid silicate phases under the high temperature, low pressure conditions at which core segregation is considered to have originated [2]. Oxygen fugacity was varied from 2 to 6 log units below the iron–wüstite (IW) buffer by increasing the Si content of the metallic phase from 100 ppm up to the 8% proposed by Allègre et al. [8] as being cosmochemically required in the earth's core. We find that Si and S, two of the principal candidates for the light element in the core are mutually exclusive in the metal phase. As oxygen fugacity is reduced, Si becomes increasingly siderophile and S increasingly lithophile. At 8% Si in the metal, all S, up to at least 1%, enters the coexisting ultramafic liquid. Thus, Si and S are incompatible during a single-stage low pressure core formation event. Mn and Cr, which are lithophile under oxidising conditions, become slightly siderophile if there is 8% Si in the metal, corresponding to an oxygen fugacity of about 6 log units below the iron–wüstite (IW) buffer. Ti remains lithophile even under these conditions, only becoming siderophile at about 7 log units below IW. These results demonstrate that the Mn and Cr contents of the core proposed in [8], coupled with lithophile behaviour of Ti, are consistent with core segregation under strongly reducing conditions. Such conditions could not generate a core containing 2% S, however, and the problem of the high contents of oxidised Fe, Ni, Co and other siderophile elements in the mantle would remain. The only plausible way of introducing S into the core is to add it as part of a late-stage accretion of oxidised material to the earth. A second, minor phase of core segregation under oxidising conditions would supply S, but no additional Si, to the core. © 1997 Elsevier Science B.V.

Keywords: partitioning; sulfur; silicon; core

1. Introduction

The Earth's core is metallic and substantially denser than the surrounding mantle. Based on core density, experimental equation of state data and cosmic abundances of the elements, the core appears to be predominantly composed of iron alloyed with

about 5 wt% Ni. Shock wave data [1] demonstrate, however, that core density is about 8–12% below that of Fe–Ni alloy under similar pressure–temperature conditions. This observation implies the presence of about 10% of one or more low atomic number elements in the liquid outer core. The nature of the light element(s) has been the subject of considerable speculation, not least because of its bearing on the overall bulk composition of the Earth, the conditions under which the core formed and its

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subsequent thermal evolution, and the processes currently operating at the core–mantle boundary. Despite this interest the sequence of events during core formation are chemically poorly constrained, so the identities of the light element(s) are still uncertain.

Although any element with atomic number lower than Fe could have the effect of reducing core density, there are a number of other important criteria [2]. Candidate elements must be of high cosmic abundance and must be sufficiently soluble in liquid Fe–Ni alloys under outer core conditions. Models of earth accretion and core segregation indicate, however [2], that the core started to segregate when the earth reached about 25% of its current radius and pressures were relatively low. Candidate light elements should also, therefore, partition into liquid Fe under the low pressure (0–5 GPa)–high temperature conditions of this early segregation. These criteria restrict the likely candidates to Si, S, O, C and H. Oxygen is unlikely to be important because of its very low solubility in liquid Fe under both low- and high-pressure conditions [3]. A recent analysis of carbon solubility in liquid Fe and the high pressure phase diagrams for carbon-bearing systems [4] suggest that carbon could only provide a small part of the light element inventory, and H is generally excluded because of its high volatility. This leaves two ‘popular’ candidates, S and Si.

Silicon was initially proposed by Birch [5] and the argument followed by MacDonald and Knopoff [6] who pointed out that the mantle has a high Mg/Si ratio when compared to chondritic meteorites. As the bulk earth shows many chemical similarities to chondritic meteorites, the missing Si was assumed to be present in the core. A similar argument applies to sulphur. Murthy and Hall [7] observed that S is depleted in the earth’s mantle relative to other elements of similar volatility by several orders of magnitude. The implication is that most of the sulphur in the earth resides in the core.

Recent discussions of the geochemical behaviour of sulphur have, from different standpoints, reached similar conclusions about the sulphur content of the earth. Allègre et al. [8] used trends of element ratios in chondritic meteorites and in the silicate earth to estimate bulk earth and core compositions. They arrived at a bulk earth S content of 0.7128%, which corresponds to 2.25% S in the core. Dreibus and

Palme [9] estimated the S content of the earth from the abundance of Zn, a non-siderophile element of similar volatility. They calculate that 98% of the Earth’s S budget is present in the core, amounting to a maximum concentration of 1.7 wt% S. In either case, S could only provide about 20% of the light element content of the core, requiring at least one additional component.

From Si/Mg and Al/Mg trends of carbonaceous and ordinary chondrites, Allègre et al. [8] arrived at Si/Mg for the bulk earth of 1.10. The observed mantle ratio of 0.945 implies, following MacDonald and Knopoff [6], a significant Si content of the core. In this case a value of 7.3% Si is obtained, implying that both Si and S provide substantial contributions to the light element inventory of the core. The presence of Si in the metal phase would require conditions of high temperature and extremely low oxygen fugacity, as found in blast furnaces. Such conditions would control the siderophile and lithophile character of other important elements such as Mn, Cr and Ti, all of which could enter the metal phase under strongly reducing conditions. Thus, any assertion that substantial Si is present in the core has important chemical implications for many other elements. The same does not apply if S and C are the main light elements in the core.

Allègre et al. [8] and McDonough and Sun [10] conclude from compositional correlations that the earth’s core has higher concentrations of Mn and Cr than the mantle but that there is essentially no Ti in the core. They obtain Mn contents of about 1160 ppm in the mantle and 5820 ppm in the core while for Cr the values are 2700 and 7790 ppm, respectively. The Ti content of the mantle is estimated as 1120 ppm with a core content of zero, while for Si the values are 21.5% and 7.3%, respectively. These values provide constraints on the oxygen fugacity during core formation, since all four elements exhibit variable valence:



Thus, if the geochemical models of core composition are correct, the oxygen fugacity of core forma-

tion was too high for reaction (a) and close to the equilibrium value for (b), (c) and (d).

The most important constraints on the processes of core formation are provided by the abundances of siderophile elements such as Ni, Co, W, Re, Os and Ir in the silicate mantle. Their concentrations in the mantle are too high and, in the cases of Re, Os, Ir and other platinum group elements, their ratios too close to chondritic [8–12] to be explained by low pressure metal–silicate equilibrium. One possible explanation is that the core formed in stages (e.g. [12]) with segregation taking place at low pressure in an accreting planet in which the accreting material became progressively more oxidised with time. The final stage (1% of the mass) would have occurred after the end of core formation and would have supplied the platinum group elements to a relatively oxidised mantle [12]. An alternative model [13,14] is based on the observation that the metal–silicate partition coefficients for some siderophile elements (Co, Ni and W, for example) decrease with increasing pressure, leading to the possibility that their abundances in the silicate mantle could be explained by single-stage core formation with equilibrium being established at high pressure. In these cases the metal–silicate partition coefficients decrease to appropriate values at about 28 GPa, which would correspond to the base of an early magma ocean with a depth of 750–1100 km. Righter and Drake [15] recently showed that Re, a highly siderophile element, may also fit this high-pressure equilibrium model. In contrast, high pressure experiments on Pd [16] give the opposite result. The effect of high pressure appears to accentuate the difficulty in explaining the mantle abundance of Pd by a single-stage equilibrium event [16]. Clearly, neither the low pressure multi-stage core formation model nor the high pressure single-stage equilibrium model can, at this moment, be excluded. The consequences of both hypotheses require further exploration.

The aim of this study has been to investigate the implications of the geochemical models [8–11,10] which assign moderate concentrations of both Si and S to the core. Since entry of Si into the metal phase requires low fO_2 , variable oxygen fugacity conditions were imposed on the system by adding varying amounts of Si to the metal phase. We performed the study in the context of low-pressure core segregation

and coupled our measurements with determination of the effect of oxygen fugacity on the metal–silicate partitioning behaviour of a suite of moderately and strongly siderophile elements. An a posteriori measurement of fO_2 was then made using compositions of coexisting oxide and metal phases.

2. Experimental procedure

The starting materials in each experiment consisted of 45 wt% synthetic basalt, 45 wt% metallic iron with light element components, and 10 wt% siderophile metal mixture (Table 1). The synthetic basalt was produced by mixing and grinding the appropriate proportions of metal oxides. This mixture was then reduced in a CO–CO₂ gas-mixing furnace to convert the Fe₂O₃ to Fe²⁺-bearing silicate at the Fayalite–Magnetite–Quartz (FMQ) oxygen buffer. The metallic component consisted of Fe, Fe₈₃Si₁₇, and FeS powders mixed in varying proportions. The strongly siderophile elements were added

Table 1
Starting compositions

	MKX2	MKX1	MKX	MKX3	MK15	MK12a
Fe	40.5	29.25	0	0	29.25	0
Fe ₈₃ Si ₁₇	0	11.25	40.5	0	11.25	40.5
FeSi	0	0	0	40.5	0	0
FeS	4.5	4.5	4.5	1	0.1	1
SiO ₂	22.26	22.26	22.26	22.26	22.26	22.26
TiO ₂	0.37	0.37	0.37	0.37	0.37	0.37
Al ₂ O ₃	6.85	6.85	6.85	6.85	6.85	6.85
Fe ₂ O ₃	3.67	3.67	3.67	3.67	3.67	3.67
FeO	0.00	0.00	0.00	0.00	0.00	0.00
MnO	0.11	0.11	0.11	0.11	0.11	0.11
MgO	4.80	4.80	4.80	4.80	4.80	4.80
CaO	5.49	5.49	5.49	5.49	5.49	5.49
Na ₂ O	0.87	0.87	0.87	0.87	0.87	0.87
K ₂ O	0.11	0.11	0.11	0.11	0.11	0.11
Cr ₂ O ₃	0.23	0.23	0.23	0.23	0.23	0.23
CoO	0.23	0.23	0.23	0.23	0.23	0.23
NiO	0.23	0.23	0.23	0.23	0.23	0.23
Re	5	5	5	5	5	5
W	2	2	2	2	2	2
Ni	1	1	1	1	1	1
Co	1	1	1	1	1	1
Ta ₂ O ₅	1	1	1	1	1	1
Total	100.22	100.22	100.22	96.72	95.82	96.72

Starting compositions in wt%.

as a mixture of 50 wt% Re, 20 wt% W, 10 wt% Ni, and 10 wt% Co metal powders and 10 wt% Ta₂O₅ powder. These materials were ground together to produce an intimately mixed powder.

The capsules were constructed from 3 mm diameter MgO rod, and contained a sample volume of approximately 3.5 mm³. This was set in crushable alumina surrounded by a cylindrical graphite furnace. Pressed BaCO₃ was used as the pressure medium with a thin inner sleeve of silica glass to protect the charge from Ba contamination. All assembly components were fired at 800°C, with the exception of the capsule, which was dried in a vacuum oven at 200°C over night, and the graphite furnace which was unheated.

The experiments were run at 1750°C and 2.5 GPa for between 1 and 2 h in a piston-cylinder apparatus at the University of Bristol. Temperature was controlled by a W/Re thermocouple situated directly above the capsule. Pressure was applied gradually over a 10 min period together with a temperature ramp rate of 170°C/min. The charge was quenched by turning off power to the graphite furnace.

The quenched charges were mounted in epoxy resin, sectioned and polished for analysis. All samples were analysed using the JEOL 8600 electron

microprobe in the Geology Department at the University of Bristol. It was necessary to analyse using an electron beam rastered over a 10 µm² area, averaging between 30 and 50 analyses of each phase. Count times of 15 sec were used for the major elements with 30 sec counts for the less abundant elements. All analyses were carried out with a beam current of 15 nA and an accelerating voltage of 20 kV. The silicate phases were analysed using natural silicates and oxides as standards with pure metals and sulphides for the metallic phase. Analyses were checked against olivine (SJIO), kaersutite (KK1) pure Fe and FeS. All microprobe corrections were made using the phi-rho-z approach [17].

3. Results and discussion

Although initially intimately mixed, all samples segregated to form a large spherical bleb of metal in the centre of the charge, surrounded by silicate melt. Both metal and silicate exhibited dendritic quench textures, indicating that both had been molten during the experiment. The quenched glass was composed of two nonstoichiometric phases (Fig. 1): the interstitial material, rich in Si, Al, and Ca, and the quench crystals, rich in Mg, Si, and Al. Progressive dissolu-

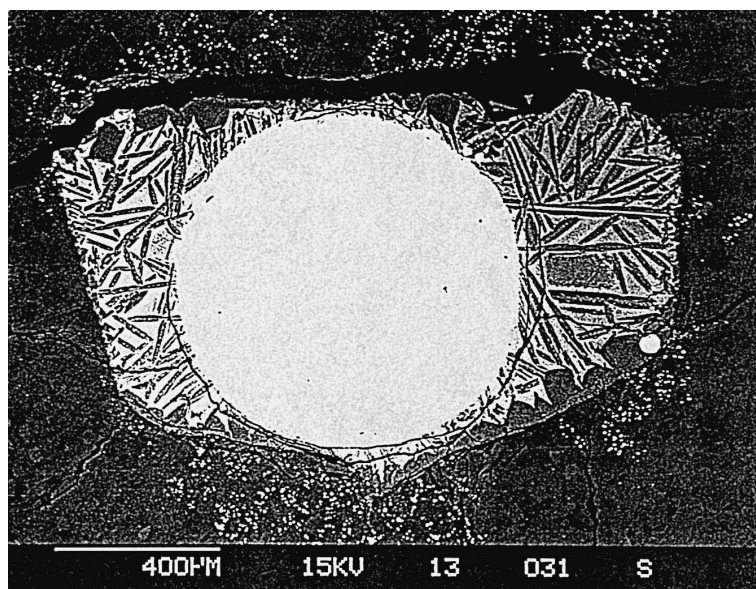


Fig. 1. Backscattered electron image of sample MKX3. The metal coalesces to form a central spherical bleb surrounded by dendritic quenched glass. The euhedral crystals at the top and bottom are olivine. The scale bar is 400 µm.

Table 2
Results

	MKX2	(±)	MKX1	(±)	MKX	(±)	MKX3	(±)	MK15	(±)	MK12a	(±)
Silicate												
No. analyses	50		61		62		45		22		20	
Na ₂ O	1.56	0.09	1.58	0.12	1.88	0.13	2.01	0.19	3.24	0.22	2.57	0.04
MgO	37.21	1.64	39.21	1.06	42.76	1.00	29.88	2.35	36.61	1.12	34.14	0.31
Al ₂ O ₃	9.66	0.92	9.23	1.35	7.23	1.06	13.99	1.53	8.76	0.63	9.13	0.53
SiO ₂	35.15	1.30	35.20	0.86	38.44	0.87	41.14	0.45	37.46	0.33	36.80	0.25
K ₂ O	0.21	0.02	0.22	0.03	0.25	0.02	0.29	0.03	0.24	0.02	0.32	0.01
CaO	9.35	0.58	10.10	0.62	8.66	0.65	12.68	0.99	9.97	0.47	13.59	0.14
TiO ₂	0.44	0.05	0.47	0.04	0.32	0.03	< 0.040	–	0.34	0.02	0.34	0.01
Cr ₂ O ₃	0.031	0.013	0.019	0.008	0.010	0.004	< 0.010	–	0.010	0.002	0.004	0.002
MnO	0.887	0.079	0.93	0.15	0.38	0.06	< 0.040	–	0.59	0.02	0.55	0.01
FeO	3.76	0.24	0.58	0.17	0.077	0.034	< 0.038	–	0.36	0.04	0.14	0.01
CoO	< 0.026	–	< 0.015	–	< 0.016	–	< 0.018	–	< 0.004	–	< 0.007	–
NiO	< 0.031	–	< 0.022	–	< 0.025	–	< 0.018	–	< 0.014	–	< 0.009	–
Ta ₂ O ₅	1.41	0.25	1.38	0.20	0.27	0.04	< 0.037	–	1.25	0.15	0.54	0.02
WO ₃	< 0.144	–	< 0.036	–	< 0.037	–	< 0.048	–	< 0.006	–	0.020	0.005
ReO ₃	< 0.073	–	< 0.066	–	< 0.053	–	< 0.035	–	0.024	0.011	0.040	0.015
S	0.21	0.07	0.99	0.30	0.98	0.34	0.72	0.08	0.04	0.005	1.80	0.05
Total	99.87		99.90		101.24		100.70		98.88		99.98	
Metal												
No. analyses	58		46		39		18		37		36	
Ti	–	–	–	–	–		0.21	0.04	–	–	–	–
Cr	< 0.002	–	0.15	0.01	0.23	0.003	0.21	0.02	0.15	0.002	0.26	0.002
Mn	< 0.011	–	0.27	0.07	1.31	0.07	1.76	0.12	0.41	0.004	1.17	0.04
Fe	78.91	0.30	80.54	0.34	72.44	0.27	56.65	0.45	80.55	0.15	76.34	0.13
Co	2.25	0.03	1.92	0.02	2.19	0.02	1.97	0.07	2.00	0.01	2.60	0.01
Ni	2.21	0.06	1.91	0.03	2.11	0.04	1.66	0.12	2.01	0.01	2.64	0.01
Ta	–	–	–	–	0.78	0.19	0.40	0.10	0.06	0.01	1.01	0.03
W	3.13	0.08	2.55	0.08	3.52	0.11	2.52	0.48	2.84	0.02	4.10	0.02
Re	10.13	0.30	8.77	0.25	8.45	0.09	8.00	0.42	7.98	0.03	3.19	0.02
Si	0.01	0.01	0.37	0.01	8.08	0.06	24.39	0.85	1.69	0.01	7.86	0.02
S	2.57	0.38	2.41	0.49	< 0.117	–	< 0.016	–	0.014	0.002	0.13	0.03
Total	99.22		98.88		99.12		97.78		97.71		99.30	
MgWüstite												
No. analyses	33		15		12		16		9		10	
MgO	89.55	0.81	94.02	3.62	96.21	0.61	96.62	0.89	94.80	0.45	94.55	0.41
Al ₂ O ₃	3.79	0.26	4.01	1.71	4.09	0.20	2.72	0.29	4.16	0.25	4.38	0.19
FeO	6.10	0.18	0.75	0.15	0.07	0.02	< 0.040	–	0.37	0.01	0.07	0.01
Total	99.44		98.78		100.37		99.34		99.33		98.99	

Electron microprobe analyses of silicate and metallic phases in wt%.

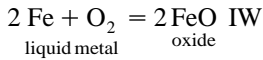
Uncertainties are taken as three standard errors.

tion of the capsule generated a layer of forsteritic olivine at the bottom of most charges (Fig. 1). The layer was found to grow with increasing run duration. Despite this, the MgO capsule remained coherent and maintained a well defined boundary with the charge, with minor absorption of Fe, Al and Mn at

the interface. A small amount of magnesiowüstite was also present at the interface between the metal and the quenched silicate. Electron microprobe analyses are presented in Table 2.

The presence of Fe-bearing MgO in the sample enables us to make a calculation of the oxygen

fugacity of the experiment from the iron (liquid)–wüstite equilibrium:



Then, relative to the IW equilibrium the oxygen fugacity is given by:

$$\log f\text{O}_2 \text{ (IW)} = 2 \log (a_{\text{FeO}}/a_{\text{Fe}})$$

where a_{FeO} and a_{Fe} are the activities of FeO in the magnesiowüstite and Fe in the metal phases, respectively. For Fe in iron-rich alloys the Raoult's Law assumption generally works well (e.g. [18]) so we assumed that the activity of Fe in the metal is equal to its mole fraction. In contrast, the magnesiowüstite in our experiments had very low mole fractions of FeO (Table 2), so it is necessary to take explicit account of activity coefficients when calculating a_{FeO} . We calculated activity coefficients using three different sets of expressions [19–21] for MgO–FeO solid solutions and found that, in all three cases, the activity coefficients for FeO are approximately 2.0. Although we selected the equations of Srecec et al. [19] for our final estimates of activity coefficient γ , all three equations yield $f\text{O}_2$ values within 0.2 log units of one another. Activity was then calculated from activity coefficient and mole fraction as follows:

$$a_{\text{FeO}} = \gamma_{\text{FeO}} X_{\text{FeO}}$$

and the result substituted into the oxygen fugacity expression above.

As anticipated, the addition of Si to the metal in reduced form has the effect of dramatically lowering

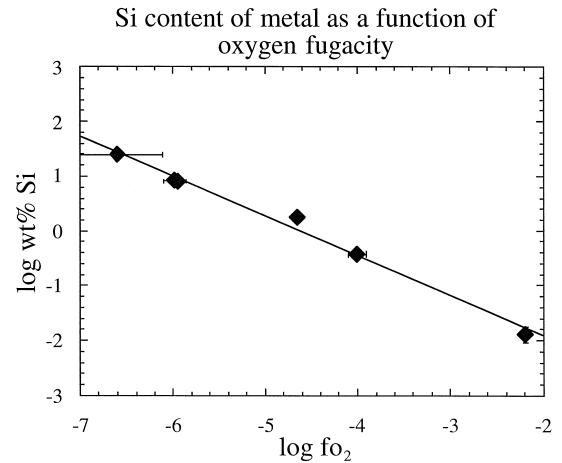


Fig. 2. Log wt% Si in the metallic phase as a function of log $f\text{O}_2$. Oxygen fugacity is expressed relative to Fe(liquid)–FeO.

the oxygen fugacity. This can be seen in Table 3 and Fig. 2. Corresponding substantial effects on the siderophile/lithophile character of the other elements were also observed.

4. Transition elements Fe, Ti, Mn, Cr, Co and Ni

As can be seen from Fig. 2, an Si content of the metal of 8% generates an $f\text{O}_2$ about 5.9 log units below IW. Metal–silicate partition coefficients (Table 3) for Fe, Ni and Co are much too high under these conditions to explain the observed abundances in the silicate mantle (Fig. 3). Iron contents could be explained if the $f\text{O}_2$ of core–mantle equilibrium

Table 3
Partition coefficients

	MKX2	(±)	MKX1	(±)	MKX	(±)	MKX3	(±)	MKX15	(±)	MK12a	(±)
$f\text{O}_2$ (IW)	−2.19	0.02	−3.99	0.10	−5.98	0.12	< −6.59	—	−4.63	0.02	−5.95	0.05
Si	−3.10	0.24	−1.64	0.03	−0.35	0.01	0.10	0.02	−1.02	0.01	−0.34	0.00
S	1.09	0.20	0.38	0.23	< −1.12	—	< −1.66	—	−0.23	0.13	−0.96	0.13
Cr	< −1.16	—	1.06	0.31	1.75	0.52	> 1.86	—	1.35	0.10	1.95	0.31
Mn	< −1.94	—	−0.43	0.23	0.65	0.10	> 1.87	—	−0.04	0.02	0.44	0.03
Fe	1.43	0.03	2.25	0.15	3.08	0.25	> 3.56	—	2.45	0.05	2.84	0.03
Co	> 2.26	—	> 2.51	—	> 2.49	—	> 2.48	—	> 2.87	—	> 2.71	—
Ni	> 2.21	—	> 2.30	—	> 2.27	—	> 2.47	—	> 2.27	—	> 2.59	—
Ta	—	—	—	—	0.55	0.21	> 1.51	—	−1.22	0.15	0.36	0.03

Metal/silicate partition coefficients calculated from log $D(\text{metal/silicate})$ in wt%.

Oxygen fugacity is relative to the iron–wüstite buffer. Uncertainties are taken as three standard errors.

were about 2 log units below IW, but under these conditions the metal would contain only of the order of 100 ppm Si. Unlike Ni and Co, Mn and Cr exhibit substantial changes in chemical behaviour as fO_2 decreases. At IW – 2.2 log units, both Mn and Cr are lithophile, while at IW – 5.9 they are quite strongly siderophile, as shown in Fig. 4. Metal–silicate partition coefficients derived from bulk silicate earth abundances of Mn and Cr [8], plotted in Fig. 3, correspond to a required core–mantle equilibrium fO_2 of –5.7 and –4.2 log units, respectively. The apparent Mn and Cr contents of the core could, therefore, be explained by equilibrium core separation under strongly reducing conditions, with an Si content of the metal on the order of 8 wt%.

One of the questions surrounding core separation under strongly reducing conditions is the behaviour of Ti. All cosmochemical models indicate that the ratio of Ti to other refractory lithophile elements in the mantle is chondritic. It has been considered (e.g. [8]) that, if core formation took place under strongly reducing conditions, then Ti could become siderophile and partition into the core. We find that Ti remains lithophile at all oxygen fugacities above 6.6 log units below IW, and only becomes siderophile under conditions when the metal contains 24% Si (IW – 6.6).

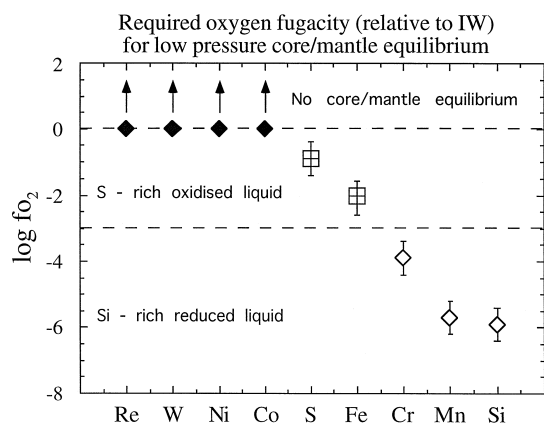


Fig. 3. The oxygen fugacity which would be required for single-stage mantle–core equilibrium based on the elemental mantle abundances of Allègre et al. [8]. Arrows indicate equilibrium under conditions too oxidising for metal to be stable. Fe and S equilibrium could be achieved under moderately oxidising conditions while Cr, Mn, and Si require strongly reducing conditions. This illustrates that, at low pressure, more than one phase of core formation would be required to explain mantle abundances.

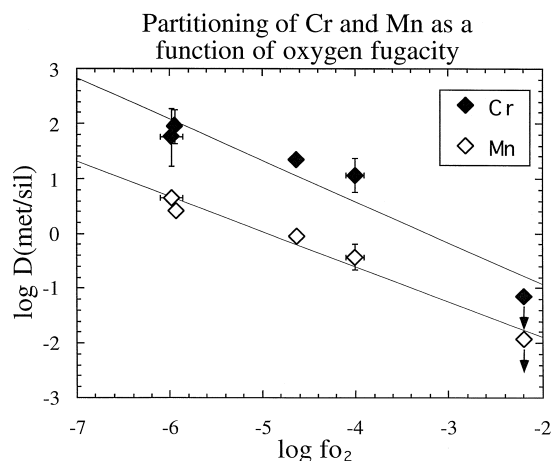


Fig. 4. Partitioning behaviour of Cr and Mn as a function of oxygen fugacity. Both elements become moderately siderophile under strongly reducing conditions. The transition from lithophile to siderophile occurs at $\log D = 0$. Arrows indicate that the D value is highly uncertain and the true value should lie in the indicated direction.

The abundances of the first-row transition elements in the mantle are clearly, therefore, not consistent with low pressure equilibrium between mantle and core. Rather, they would require core separation under reducing conditions, removing some Mn and Cr, but no Ti, followed by later addition of oxidised material to the earth [15] to provide oxidised Fe, Ni and Co to the mantle.

5. Ta, W and Re

As expected, Re was largely unaffected by changes in fO_2 at low pressure and remained highly siderophile in all experiments. W, a ‘moderately’ siderophile element, also appeared highly siderophile under the reducing conditions employed in this study. Ta becomes somewhat siderophile under the most reducing conditions. In all three cases, the low pressure data would require multi-stage core segregation to explain mantle abundances.

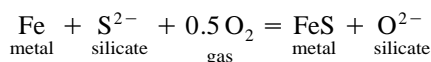
6. Sulphur and silicon in the metal

The most striking observation from these experiments is the incompatibility of sulphur and silicon in

the segregating liquid metal. The behaviour of S is illustrated in Fig. 5, where the logarithm of the metal/silicate partition coefficient for sulphur, D , is plotted against $\log fO_2$. A clear decrease in D with decreasing fO_2 can be seen. This means that, as fO_2 is lowered to the point where significant amounts of Si enter the metal, S becomes lithophile and remains in the silicate melt. Thus Si and S are mutually incompatible during core formation.

Although liquid immiscibility is encountered in the system Fe–Si–S at low pressure (e.g. Poirier [22]) the metal concentrations of Si and S obtained in our study are well within the one-phase miscible region. As expected, therefore, no immiscible S-rich liquid was found in our experiments. The distinctive incompatible behaviour of Si and S which we observe is due predominantly to the dependence of metal–silicate partitioning behaviour on fO_2 and has no direct link to immiscibility in the Fe–Si–S metal phase.

The apparent incompatibility of Si and S during metal segregation is also observed in metallurgical operations, where most of the sulphur enters the silicate slag [23]. Chemically, it can be explained by equilibria of the type:



At high oxygen fugacity S resides as FeS in either

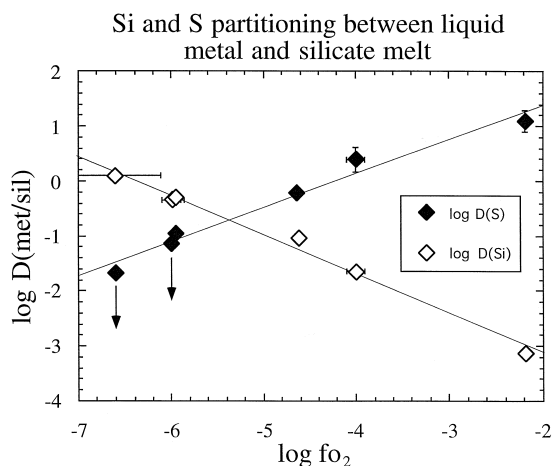


Fig. 5. Partitioning behaviour of S and Si between liquid metal and liquid silicate as a function of fO_2 . S becomes lithophile ($\log D < 0$) under conditions reducing enough to allow significant amounts of Si to enter the metallic phase.

liquid sulphide or liquid metal. As fO_2 is decreased then S enters the silicate melt as sulphide, S^{2-} species [24], and the metal becomes S-poor. What we find here is that, with silicate melt close in composition to the mantle (Table 1), the equilibrium is fully to the left under conditions of fO_2 where Si can enter the metal. Thus, S^{2-} remains in the silicate and S and Si are incompatible in the metal phase.

From the observed behaviour of S the bulk earth abundances [9] would require an fO_2 of 0.8 log units below IW. Given an S content of about 2% in the core, either the latter contains no Si and was formed under oxidising conditions or the S was added later as an oxidised component [12].

7. Conclusions

Partitioning behaviour of the moderately siderophile elements Cr, Mn and Ti between metal and silicate melt is strongly dependent on the fO_2 of equilibrium. If we fix fO_2 at a low value and assume that when the earth's core formed it contained about 8% Si, as suggested by recent geochemical models, then the following behaviour is observed:

1. The Si content of the metal increases dramatically with decreasing fO_2 from close to zero at 2 log units below the IW buffer to 8 wt% at 5.9 log units below.
2. Ti remains lithophile to about 6 log units below IW. Thus, the observed chondritic ratio of Ti to other refractory lithophile elements in the earth would be consistent with a core containing 8% Si.
3. Cr and Mn change from lithophile to siderophile elements as the fO_2 is reduced from 2.2 to 5.9 log units below the IW buffer. The abundances of these two elements in the mantle [8,10] are consistent with part of the earth's budget of them having been partitioned into a segregating, Si-rich metal under strongly reducing conditions.
4. Ni, Co and Fe are strongly siderophile at 5.9 log units below IW and their abundances in the mantle cannot be explained by single-stage low pressure core–mantle equilibrium.
5. As fO_2 decreases S becomes increasingly lithophile. This means that the observed depletion

of the silicate mantle in S relative to other volatile elements cannot be explained by equilibrium under strongly reducing conditions. Under such conditions all of the S would remain in the mantle and no depletion relative to elements of comparable volatility would be observed. S and Si are thus mutually incompatible in the metal during core formation.

Assuming that core separation initiated under relatively low pressure conditions these observations can be reconciled with a core containing 8% Si and 2% S if the major event of core segregation occurred under strongly reducing conditions. This would have removed Si, Fe, Ni, Co, W, Re and most of the Mn and Cr to the core. Later addition of oxidised material would have added an FeS-rich liquid to the core together with oxidised Fe, Ni and Co to the mantle. Provided that core composition remained within the miscible region in the Fe–Si–S phase diagram [22], addition of FeS would not require that Si be expelled since S and Si are only incompatible when the metal is in equilibrium with silicate melt. Given its small area/volume ratio and isolation through the D'' layer, the core can plausibly be considered to be chemically isolated from the mantle and hence unlikely to expel Si as FeS is added to it.

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